

Pressure-driven metal-insulator transition in BiFeO₃ from Dynamical Mean-Field Theory

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A metal-insulator transition (MIT) in BiFeO₃ under pressure was investigated by a method combining Generalized Gradient Corrected Local Density Approximation with Dynamical Mean-Field Theory (GGA+DMFT). Our paramagnetic calculations are found to be in agreement with experimental phase diagram: Magnetic and spectral properties of BiFeO₃ at ambient and high pressures were calculated for three experimental crystal structures *R3c*, *Pbnm* and *Pm3m*. At ambient pressure in the *R3c* phase, an insulating gap of 1.2 eV was obtained in good agreement with its experimental value. Both *R3c* and *Pbnm* phases have a metal-insulator transition that occurs simultaneously with a high-spin (HS) to low-spin (LS) transition. The critical pressure for the *Pbnm* phase is 25–33 GPa that agrees well with the experimental observations. The high pressure and temperature *Pm3m* phase exhibits a metallic behavior observed experimentally as well as in our calculations in the whole range of considered pressures and undergoes to the LS state at 33 GPa where a *Pbnm* to *Pm3m* transition is experimentally observed. The antiferromagnetic GGA+DMFT calculations carried out for the *Pbnm* structure result in simultaneous MIT and HS-LS transitions at a critical pressure of 43 GPa in agreement with the experimental data.

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I. INTRODUCTION

Multiferroics are used in various applications for energy production, transmission of high voltage lines, data storage devices, and sensors¹. They will help to replace a number of currently used lead-based materials which contain lead toxic and harmful to the environment. One of the most promising candidates for applications, bismuth ferrite BiFeO₃, is actively studied because of the coupling between ferroelectric and magnetic order around room temperature in this compound. Recent investigations of BiFeO₃ at high pressures up to 60 GPa reveal metal-insulator² and high-spin to low-spin (HS-LS) transitions³ in Fe³⁺ at room temperature in a relatively wide pressure range 40–55 GPa accomplished by the structural phase transition⁴.

The problem becomes even more complicated taking into account that BiFeO₃ has a rich phase diagram. At ambient pressure and up to 1100 K it has rhombohedral (*R3c*) crystal structure¹¹. Increasing temperature and pressure, the structure of BiFeO₃ transforms into orthorhombic *Pbnm*¹² and then cubic *Pm3m*¹³.

For many years, metal-insulator transition (MIT) in *d* or *f* metal compounds⁵ is one of the central issues in condensed matter physics. The most spectacular examples are pressure-driven transitions from a wide gap Mott insulator to metallic state in transition metal oxides. For MnO and Fe₂O₃ (*d*⁵ configuration), the metal-insulator transition is accompanied by the high-spin to low-spin (HS-LS) transition.

Recently, these and other MITs and spin transitions were successfully described theoretically^{7–10} employing

the method combining density functional approximations (like, GGA or LDA) with dynamical mean-field theory⁶. Pressure-driven MIT correlated with magnetic collapse could be treated as a delocalization of magnetic electrons or structural phase transition into new phase with Néel point below room temperature¹⁵.

Another Mott-type mechanism controlled by dramatic U_{eff} decrease due to HS-LS transition was proposed in Ref.². Mott-type MIT driven by a broadening of the t_{2g} states was confirmed by the LDA+*U* calculations which revealed the HS-LS transition at 36 GPa and a transition to the metallic phase with no localized moment above 72 GPa¹⁶.

In this paper we investigate the properties of BiFeO₃ under pressure employing the method accounting for dynamical electronic correlations and considering three experimental crystal structures.

II. METHOD

The GGA+DMFT method⁶ is realized in a computational scheme constructed in the following way: first, a Hamiltonian \hat{H}_{GGA} is produced using converged GGA results for a compound under investigation, then the many-body Hamiltonian is set up, and finally the corresponding self-consistent DMFT equations are solved. In this work the Hamiltonians \hat{H}_{GGA} are constructed in a Wannier function (WF) basis^{18,19} using the projection procedure described in detail in Ref. 20. Initial ab-initio calculations of the electronic structure are done within the pseudo-potential plane-wave method, as implemented in

Quantum ESPRESSO¹⁷.

The WFs are defined by the choice of Bloch functions Hilbert space and by a set of trial localized orbitals that will be projected on these Bloch functions. The basis set includes all bands that are formed by O 2*p* and Fe 3*d* states and correspondingly the full set of the O 2*p* and Fe 3*d* atomic orbitals to be projected on Bloch functions for these bands. That would correspond to the extended model where in addition to the *d* orbitals all *p* orbitals are also included.

The resulting *p*–*d* Hamiltonian to be solved by DMFT has the form

$$\hat{H} = \hat{H}_{GGA} - \hat{H}_{dc} + \frac{1}{2} \sum_{i,\alpha,\beta,\sigma,\sigma'} U_{\alpha\beta}^{\sigma\sigma'} \hat{n}_{i\alpha\sigma}^d \hat{n}_{i\beta\sigma'}^d, \quad (1)$$

where $U_{\alpha\beta}^{\sigma\sigma'}$ is the Coulomb interaction matrix, $\hat{n}_{i\alpha\sigma}^d$ is the occupation number operator for the *d* electrons with orbitals α or β and spin indices σ or σ' on the *i*-th site. The term \hat{H}_{dc} stands for the *d*–*d* interaction already accounted for in GGA, so called double-counting correction. In the present calculation the double-counting was chosen in the following form $\hat{H}_{dc} = \bar{U}(n_{dmft} - \frac{1}{2})\hat{I}$. Here n_{dmft} is the self-consistent total number of *d* electrons obtained within GGA+DMFT, \bar{U} is the average Coulomb parameter for the *d* states, and \hat{I} is unit operator.

The elements of $U_{\alpha\beta}^{\sigma\sigma'}$ matrix are parameterized by U and J_H according to the procedure described in²¹. The values of Coulomb repulsion parameter U and Hund exchange parameter J_H were calculated by the constrained LDA method²² on Wannier functions²⁰. The values $U=6$ eV and $J_H=0.93$ eV obtained in these calculations are close to the previous estimations^{16,23}. The effective impurity problem in DMFT was solved by the hybridization expansion Continuous-Time Quantum Monte-Carlo method (CT-QMC)²⁴. The calculations for all volumes were performed in the paramagnetic state for inverse temperature $\beta = 1/T=15$ eV^{−1} corresponding to 770 K. According to the phase diagram, no long-range ordering in BiFeO₃ was found in this temperature region. The spectral functions on real energies were calculated employing Maximum Entropy Method (MEM)²⁵.

III. RESULTS AND DISCUSSION

In all structures under investigation iron is surrounded by oxygen ions forming an octahedron. In the high pressure cubic $Pm\bar{3}m$ phase, the Fe *d* band is split by crystal field into threefold degenerate t_{2g} and twofold degenerate e_g sub-bands. A trigonal distortion in the *R3c* structure lowers the point symmetry group O_h to D_{3h} , so that threefold degenerate t_{2g} becomes split into twofold degenerate e_g^π and non-degenerate a_{1g} band. The *Pbnm* structure has the lowest symmetry and all orbitals become nonequivalent but still three groups of orbitals could be considered: e_{g1}^σ and e_{g2}^σ , e_{g1}^π and e_{g2}^π and a_{1g} . For simplicity we will use cubic t_{2g} and e_g orbitals notations for analysis hereafter.

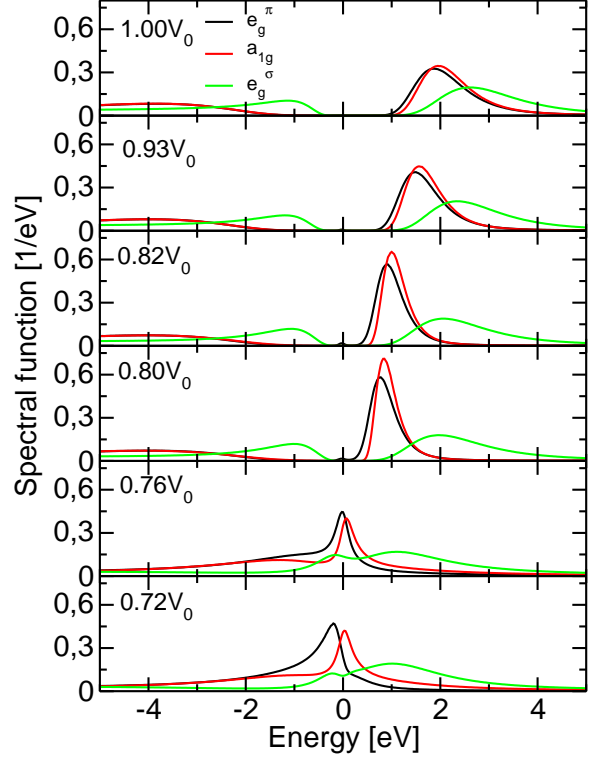


FIG. 1: (Color online) Spectral function of Fe *d* states for different volumes related to the ambient pressure volume V_0 obtained in the GGA+DMFT (CT-QMC) calculations for the low pressure *R3c* phase at 770 K.

Previous calculations demonstrated that LDA fails to describe an insulating character of the BiFeO₃ ground state at ambient pressure and for all volumes it is metallic in all structures. However, a gap of the AFM origin was obtained in the GGA calculation made for several magnetic structures²⁶.

Our GGA+DMFT calculations produced for the *R3c* phase of BiFeO₃ show that taking into account Coulomb correlation effects results a wide-gap Mott insulator and high-spin state for ambient pressure in agreement with the experimental data. The obtained spectral functions for different cell volumes are shown in Fig. 1. The calculated energy gap value of about 1.2 eV agrees well with the experimental value of 2.4 eV for direct optical gap^{27,28} and 1.8 eV indirect optical gap at AP²⁹ at room temperature and indirect gap value 1.3 eV measured in thin films³¹, 1.5 eV at 820K³⁰. The magnitude of magnetic moment $\sqrt{\langle m_z^2 \rangle}$ is $4.6\mu_B$ at AP. This number agrees very well with the high-spin state of the Fe⁺² ion (d⁵ configuration) in cubic crystal field: 2 electrons in the e_g band and 3 electrons in the t_{2g} band with the magnetic moment value of $5\mu_B$. Then the magnetic moment decreases and at $0.76V_0$ drops down to $2.5\mu_B$, and it equals to $2.0\mu_B$ when the volume is $0.72V_0$ (63 GPa). The later value is close to the one expected for the LS state with

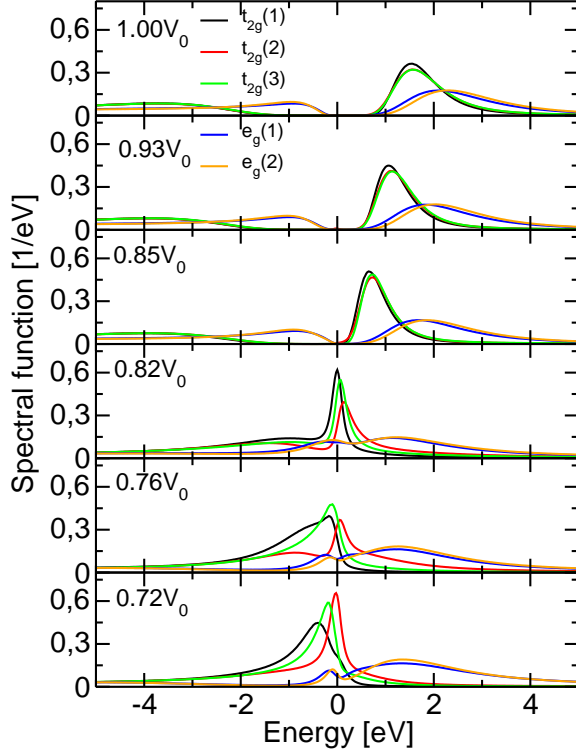


FIG. 2: (Color online) Spectral function of Fe-d states vs. volume reduction obtained in GGA+DMFT (CT-QMC) calculations for the *Pbnm* phase at 770K.

5 electrons in the t_{2g} band but strong hybridization between iron and oxygen leads to the non zero occupation of the e_g orbitals. This mechanism was obtained in all three crystal structures and is considered in detail for the *Pbnm* case.

The most interesting phase is *Pbnm* since both the HS-LS and metal-insulator transitions occur simultaneously with the *Pbnm* to *Pm3m* phase transition. The GGA+DMFT spectral functions for different cell volumes are shown in Fig. 2. Note, that the *Pbnm* phase doesn't exist to 2 GPa at 770 K. But BiFeO₃ in the *Pbnm* structure and experimental with cell volume of *R3c* at ambient pressure is an insulator with a gap of 1 eV which is close to the experimental data²⁸⁻³⁰. When the cell volume is $0.85V_0$ the gap is closed but iron is still in the HS state (see Fig. 3) that contradicts to the mechanism proposed in Ref. 2. Then together with the volume decrease the t_{2g} occupancy increases and both magnetic moment and a number of e_g electrons shrink. Both transitions don't appear to happen instantly but have a crossover region $0.85-0.82V_0$ that agrees with the experimental observations^{2,3,14}.

MIT at room temperature where long range order exists occurs in the pressure range 45-55 GPa. In order to reproduce the temperature dependence of critical pressure value the paramagnetic GGA+DMFT calculation

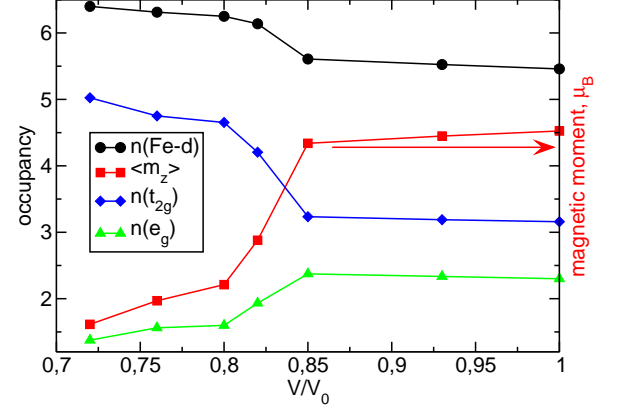


FIG. 3: (Color online) Magnetic moments (red square), occupancy of the d states (black circles), t_{2g} (blue diamonds), and e_g (green triangles) states obtained in the GGA+DMFT (CT-QMC) calculations for the *Pbnm* phase.

for $\beta=40\text{eV}^{-1}$ eV was carried out. The results obtained show that at 33 GPa BiFeO₃ is already in the metallic LS state as well as at higher temperature. Hence increase of the critical pressure isn't a temperature-driven effect. Then we have carried out magnetic GGA+DMFT calculation for the same cell volumes of *Pbnm* structures. Small external magnetic field 0.01 eV was applied to each Fe atom so that direction of the field on sites corresponds to experimentally observed G-type AFM. The gap value increases slightly but more important magnetic solution was stabilized and MIT occurs between $0.82-0.8V_0$ that corresponds to 33-43 GPa. This value is close to transition pressure 45-55 GPa measured at 300 K in AFM phase.

Probabilities of charge and orbital configurations measured in the GGA+DMFT method within impurity solver are shown in Fig.5. The hybridization between iron and oxygen and hence the d states occupation increases with the volume contraction. At ambient pressure, the d^5 configuration has the larger impact but the d^6 probability is also sizable. With the volume reduction probabilities of d^6 and d^7 configurations grow up and the probability of the d^5 configuration shrinks, see the upper panel of Fig.5.

More detailed picture of orbital configuration impacts is shown in Fig. 5 (lower panel). One can see that the probabilities of the HS configuration with any number of electrons (d^5 , d^6 and d^7) which dominate at ambient pressure goes down and after the cell volume become smaller than $0.85V_0$ drops and LS and IS configuration probability increase.

The calculation carried out for the high temperature cubic *Pm3m* phase demonstrates that for all experimental volumes BiFeO₃ has a metallic behavior. The high spin to low spin state transition was also obtained in the calculation for the *Pm3m* phase at $0.8V_0$ (33 GPa).

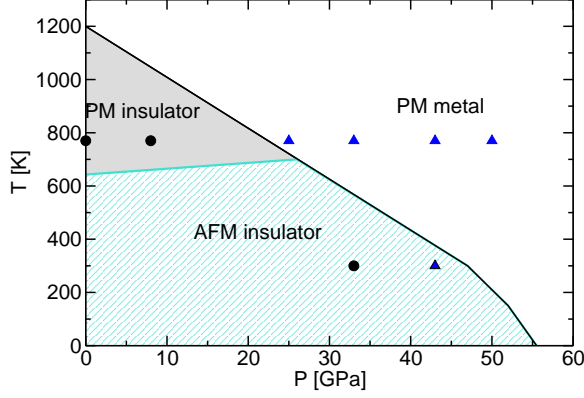


FIG. 4: (Color online) Combined phase diagram of BiFeO_3 . Experimental data taken from Ref.14 are shown with solid lines. Insulator and metallic solutions obtained in GGA+DMFT calculation are shown with black squares and blue triangles, correspondingly. Critical pressure obtained in paramagnetic calculation is 25 GPa. Spin polarized GGA+DMFT results at 300 K results in IMT in a range 33-43 GPa.

IV. IN CONCLUSION

We have performed the GGA+DMFT calculations for BiFeO_3 at 700 K where it has no long range order for a number of different cell volumes corresponding to the whole range of experimentally applied pressures (from ambient pressure up to 60 GPa). In agreement with experiments, the spectral functions for BiFeO_3 in the $R3c$ phase as well as in $Pbnm$ at ambient pressure demonstrates an energy gap of about 1.2 eV in a good agreement with experiment. When the unit cell volume is 0.85-0.82 V_0 that corresponds to 25-33 GPa BiFeO_3 in the $Pbnm$ crystal structure becomes metallic, and, simultaneously, its magnetic moments shrink. In the low pressure $R3c$ structure, the same transition occurs in cell with the smaller volume 0.8-0.76 V_0 (40-50 GPa). The high pressure cubic $Pm\bar{3}m$ phase is metallic in the whole range of the investigated pressures (cell volumes) but the HS-LS transition also takes place when the cell volume is smaller than 0.82 V_0 (33 GPa). The higher critical pressure of 43 GPa was obtained in the AFM GGA+DMFT calculations for the $Pbnm$ structure in good agreement with the experimental phase diagram.

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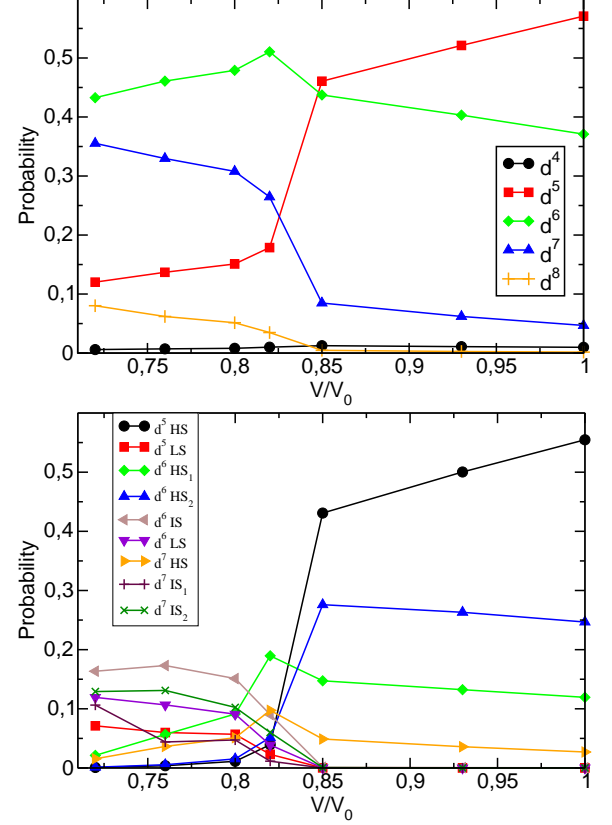


FIG. 5: (Color online) Probabilities of different charge states d^n (upper panel) and orbital configurations of Fe ion (lower panel) vs. pressure obtained in the GGA+DMFT (CT-QMC) calculations for $Pbnm$ phase (shown only largest ones): d^5 -HS (up: $t_{2g}^3 e_g^2$, down: $t_{2g}^0 e_g^0$), d^5 -LS (up: $t_{2g}^3 e_g^0$, down: $t_{2g}^2 e_g^0$), d^6 -HS₁ (up: $t_{2g}^3 e_g^2$, down: $t_{2g}^1 e_g^0$), d^6 -HS₂ (up: $t_{2g}^3 e_g^2$, down: $t_{2g}^0 e_g^1$), d^6 -LS (up: $t_{2g}^3 e_g^1$, down: $t_{2g}^2 e_g^0$), d^7 -HS (up: $t_{2g}^3 e_g^2$, down: $t_{2g}^1 e_g^1$), d^7 -LS₁ (up: $t_{2g}^3 e_g^1$, down: $t_{2g}^2 e_g^0$), d^7 -LS₂ (up: $t_{2g}^3 e_g^1$, down: $t_{2g}^2 e_g^1$).

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